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Study on Growth Mode and Properties of Electroless Nickel Plating on Aluminum Alloy

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In this paper, Ni-P alloy coating was prepared by electroless nickel plating with alkaline plating-acid plating double solution system on aluminum alloy 6061 sheet. This paper mainly studies the changes of coating morphology after pretreatment in different alkaline plating baths and the properties of the electroless nickel plating after different time plating in the acidic chemical plating bath, analyze the experimental results, use scanning electron microscopy (SEM) to observe the surface morphology of the samples, and use EDS determine the coating composition, then obtained the growth pattern of the electroless nickel plating layer on aluminum alloy, test the properties of the coating, and the surface roughness, adhesion, microhardness and porosity of the coating were measured.

1. Introduction

With the continuous progress of electroless nickel plating on aluminum and aluminum alloy, the application of electroless nickel plating on aluminum products is more and more popular, from the point of view of metal products, its quantity is only second to steel. Aluminum material has samll density, thermal conductivity, good conductivity, high strength to weight ratio, and processing and molding convenient, which has been widely used, but its existence is easy to corrosion, not wear, welding and other shortcomings, thus it should be based on the need to use the appropriate surface treatment. Electroless nickel plating is one of the ideal surface modification technologies for aluminum and aluminum alloys. It cannot only improve the corrosion resistance, wear resistance, weldability, but also through the chemical plating of different nickel-based alloys, aluminum and aluminum can be given a variety of new features, such as magnetic properties, lubrication performance, brazing performance. Aluminum is a hard-to-plated metal substrate. Because aluminum has a strong affinity for oxygen, the aluminum surface is highly prone to oxide film formation, even if the chemical removal, in the plating of other metals before the formation of new oxide film. This oxide film and the coating adhesion is poor. In addition, the standard electrode potential of aluminum is very negative (-1.66V), in the bath is easy to replace the metal ions with a positive displacement reaction generated loose layer, affecting the coating adhesion. Therefore, in order to get the combination of aluminum surface and excellent performance of the nickel layer, pre-plating is the key. At present, domestic and foreign research to solve this problem can be summarized into three kinds of technical approaches: (1) Zinc-pre-plating method; (2) anodic oxidation method; (3) direct chemical nickel plating. So far, the research and development and application of the process has been relatively focused on the use of dip zinc pre coating method. The main disadvantage of zinc immersion method is in the humid corrosive environment, the zinc is an anode relative to the nickel plating, it will be subject to lateral corrosion, eventually leading to nickel layer peeling. In addition, low melting point of the transition zinc layer limits the scope of application, but also between the two zinc dip zinc nitrate process there is a pollution of the production environment. The dip layer also contaminates the electroless nickel plating solution. At present, the goods dip zinc alloy containing cyanide, caused great harm, and does not meet environmental requirements. Electrolessnickel coating with plain and high binding force was obtained in this experiment. the samples were heat treated and diffused, then microstructure and transformation was investigated by optical microscope and scanning electron microscope. The hardness, binding force, wear and corrosion resistance are tested, the reasonable heat treatment process is gained. Hardness is increased after eletroless nickel plating and heat treatment compared with the matrix. The adhesion of sample heat treated at

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400℃ is highest, the weight loss and friction coefficient is lowest, the corrosion resistance is best. Electroless nickel plating is widely used in aluminum alloys, such as in computer and electronic equipment, military and plastic mold on the application.Electroless plating first began in electroless nickel plating, now it has been developed to electroless copper, electroless cobalt, electroless tin and electroless gold, silver, platinum and other precious metals and multi-alloy. Electroless nickel-boron baths reduced with sodium borohydride can be stabilized with various agents such as thallium nitrate or lead tungstate with no fundamental modification of deposition rates and stability. To improve the mechanical properties of electroless nickel-boron deposits, various heat treatments are applied. At low temperatures, no fundamental changes in the deposit structure are observed, only an improvement of adhesion on aluminium substrate. The values of the Knoopmicrohardness obtained on these heat-treated deposits are near 600 hk100. At higher temperatures, structural changes take place and the nickel-boron deposits crystallize. The microhardness rises until 1050 hk 50 for heat treatments at 350 °C for 4 h. A diffusion layer between the electroless nickel deposit and the aluminium substrate appears at high heat treatment temperatures. The results of scratch tests show that the Ni-B deposits, with or without heat treatments, have good tribological properties under external solicitations. They are hard, wear and abrasion resistant, and also have good adhesion to the aluminium substrate.At present, electroless nickel plating has been widely used in various industrial sectors such as electronics, computer, machinery, transportation, energy, oil and gas, chemical and chemical industry, aerospace, automobile, mining, food machinery, printing, mold, textile and medical equipment. According to the classification of electroless nickel base materials, the largest substrates on the market are carbon steel and cast iron, about 71%, aluminum and non-ferrous metals accounted for 20%, 6% alloy steel, other (plastics, ceramics, etc.) accounted for only 3%.

2. Experimental method

2.1 Experimental Materials

In the experiment, aluminum alloy 6061 sheet was used as the sample material, and its main components (mass fraction) are shown in Table 1.The sample size is50mm×50mm×1mm, Surface area is 0.5 ㎡. Al6061 is Al-Mg-Siheat treatment can be strengthened aluminum alloy, alloy main strengthening phase is Mg_2Si, alloy contains a small amount of Cu and Cr, which can increase the strength of Cu, Crcan offset the adverse effects of Cuon corrosion resistance.

Table 1: The chemical constitution of 6061 alloy

Grade	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
6061	0.4~0.8	0.7	0.15~0.4	0.15	0.8~1.2	0.04~0.35	0.25	0.15	margin

In the experiment, the reagents used in the preparation of the solution were nickel sulfate, sodium hypophosphite, sodium acetate, ammonium citrate, citric acid, sodium potassium tartrate, ammonia, sodium hydroxide, zinc oxide, ferric chloride, sodium nitrate, sodium phosphate, Sodium carbonate, nitric acid, hydrochloric acid, sulfuric acid, these are commercially available analytical grade.

2.2 Experimental method

1) Sample preparation

Cut the 6061 aluminum alloy sheet to the required sample size and subjected to grinding and chamfering.

2) Sample pretreatment

Pretreatment of sample is dominant in the whole process, and the quality of pre-treatment will directly affect the quality and performance of coating. Pretreatment process which includes the main, detergent cleaning decontamination, alkali washing oil, pickling out the light and the second dip zinc.

3) Alkaline electroless nickel plating

Carry out alkalineelectroless nickel plating on the pretreated sample, and change the plating time of alkaline electroless nickel plating under the same process parameters such as temperature and pH, respectively, select the time parameters 5s, 10s, 15s, 30s, through the contrastive experiments to observe the SEM morphology of the coatings at different time periods, and carry out EDS determination to study the growth mode of the Ni-P coatings.

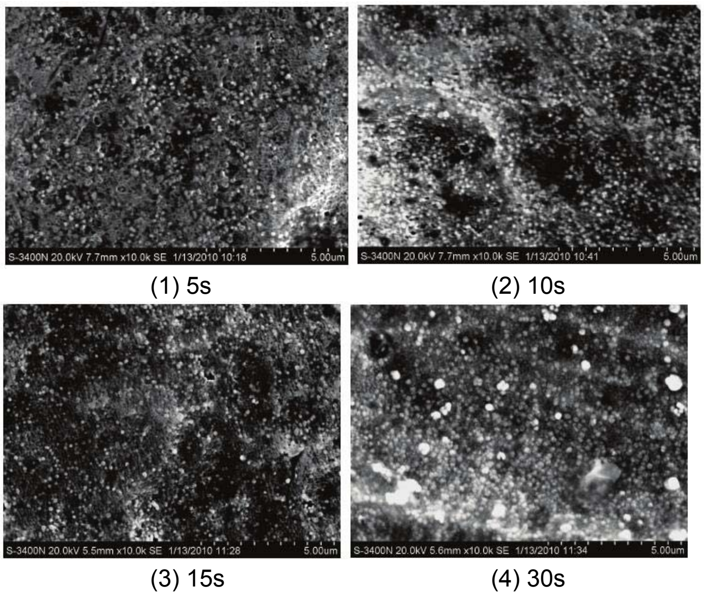
4) Acidic electroless nickel plating

After electroless plating for 5min (pre-plating nickel), the electroless nickel plating was carried out. Under the same conditions, respectively, plating 30min, 60min, 90min, and test the hardness, thickness, adhesion and other properties of the coating in each time period, study the mechanical properties and appearance of electroless nickel plating on aluminum alloy.

3. Results

3.1 Study on growth mode of electroless nickel plating on aluminum alloy

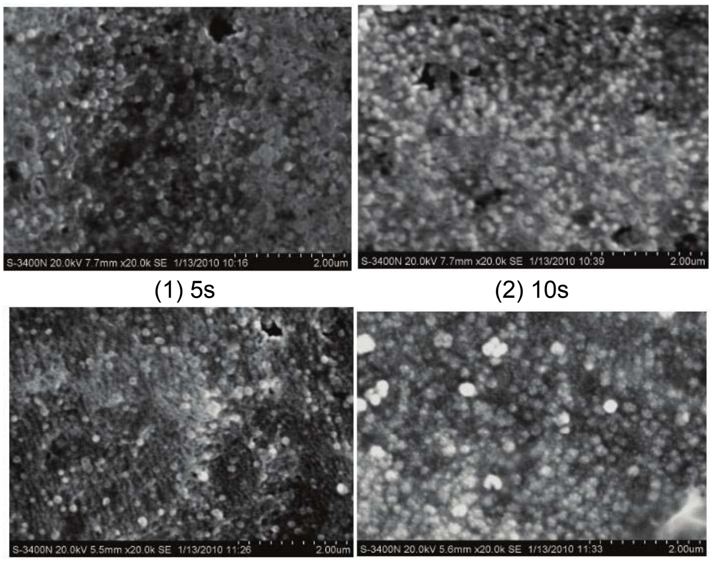
Alkaline electroless nickel plating on 6061 aluminum alloy after alkali cleaning, pickling and secondary zinc immersion treatment, by scanning electron microscopy (SEM) to observe the surface morphology of the coatings, and use EDS to detect the composition of the coating.The pH value of the alkaline solution is 9, the temperature is 45 ℃, the plating time is 5s, 10s, 15s, 30s respectively. The surface morphology of the coating is shown in Fig.1 and Fig.2.It can be seen from the figure that the amount of Ni-P particles deposited on the surface of the sample increases with the plating time. This is because, with the increase of plating time, Ni-P particles deposit on the surface of the sample, these newly deposited Ni-P particles becomes the new nucleation center to deposit Ni-P particles. Therefore, the deposition rate of the phosphorus particles is increasing until the surface is completely covered with the Ni-P plating layer.



Figures 1: Surface images of electroless Ni-P alloy plating for various deposition times at pH 9: (1) 5 s; (2) 10 s; (3) 15 s; (4) 30 s

Observe the Figure 2 (3), (4): After15s plating, the surface of the substrate is almost completely covered by the deposited Ni-P particles, after 30s plating, it find that the particles deposited on the surface of the aggregation, growth, fusion and so on.This is because, when the surface of the sample is completely covered with the Ni-P plating, the particles continue to be deposited on the surface, and a plurality of Ni-P particles are gathered, fused and grown to form a cell in the transverse direction of the substrate surface.

Figures 3 is the EDS coating to detect the energy spectrum, corresponding to Figure 1, It is found that the surface of the sample after plating has not only contains the elements of Ni and P, but also contains the elements of Zn, Al, Mg, Si and Fe, this is because the aluminum alloy 6061 belongs to the Al-Mg-Si alloy, and the sample is subjected to zinc immersion treatment before electroless plating. Through analyze the figure (1) (2) (3) (4) obtained: The content of Ni and P increases with the time of plating, and the content of Zn decreases continuously and disappears on the surface of sample after 30s.Therefore, it can be concluded that at the initial stage of electroless nickel plating, the nickel-phosphorus particles are mainly deposited at the Zn particles.It can be deduced that during the process of electroless nickel plating, the deposition of nickel-phosphorus particles occurs near the Zn particles; because of its randomness, it also occurs in the vicinity of Zn particles and the first deposited Ni-P particles.



(1) 5s (2) 10s

(3) 15s (4) 30s

Figures 2: Surface images of electroless Ni-P alloy plating for various deposition times at pH 9: (1) 5 s; (2) 10 s; (3) 15 s; (4) 30 s

3.2 Study on properties of electroless nickel plating on aluminum alloy

1) Porosity and roughness of acid plated Ni-P coatings

The porosity of electroless plating has obvious effect on the corrosion resistance of the coating.In this paper, the porosity was measured in three samples with 30min, 60min and 90min plating time respectively.From Table 2 available, the porosity of the coating with the plating time increases, the coating thickness gradually increases, the porosity gradually decreases.When the coating thickness is 25μm, the coating porosity is 0, it can be drawn that, the thicker the coating, the smaller the porosity, and corrosion resistance of the coating the better.

Table 2: Properties parameters of Ni-P coatings

Acid plating time /min	Coating surface roughness/μm	Plating thickness /m	Porosity /cm^2
0 (after degreasing)	0.808	0	/
30	0.289	10	6
60	0.231	20	1
90	0.798	25	0

Table 2 also shows the changes in coating roughness, the surface roughness of the coating is 0.808 when the surface is not plated, which is due to defects such as bumps on the surface of the coating after acid etching, leading to the coating surface roughness. After 30minplating, roughness significantly reduced, the 60min coating roughness even slightly smallerthan the 30min. Therefore, the electroless nickel surface treatment method can make the surface of the substrate become uniform and flat, the treatment method not only has the protective effect on the substrate surface, but also can increase its appearance and decoration. But whenplating 90min, the roughness of the coating becomes larger, and the roughness of the coating is almost same as the not being plated, this is because the bath has its maximum load carrying capacity, When the plating time is longer, the plating solution will be self-decomposition reaction, the plating liquid impurities and some harmful substanceswill affect the quality of the coating. So the plating solution after plating a certain period of time should be added and adjusted to extend the service life of the bath.

2) Micro-hardness of acid Ni-P plating

Table 3: Micro-hardness of the substrate and the as deposited coatings

Samples	Aluminum alloy 6061	Ni-Pcoating (30min)	Ni-Pcoating (60min)	Ni-Pcoating (90min)
Micro-hardness ($HV_{0.2}$)	108.8	228.3	412.0	624.2

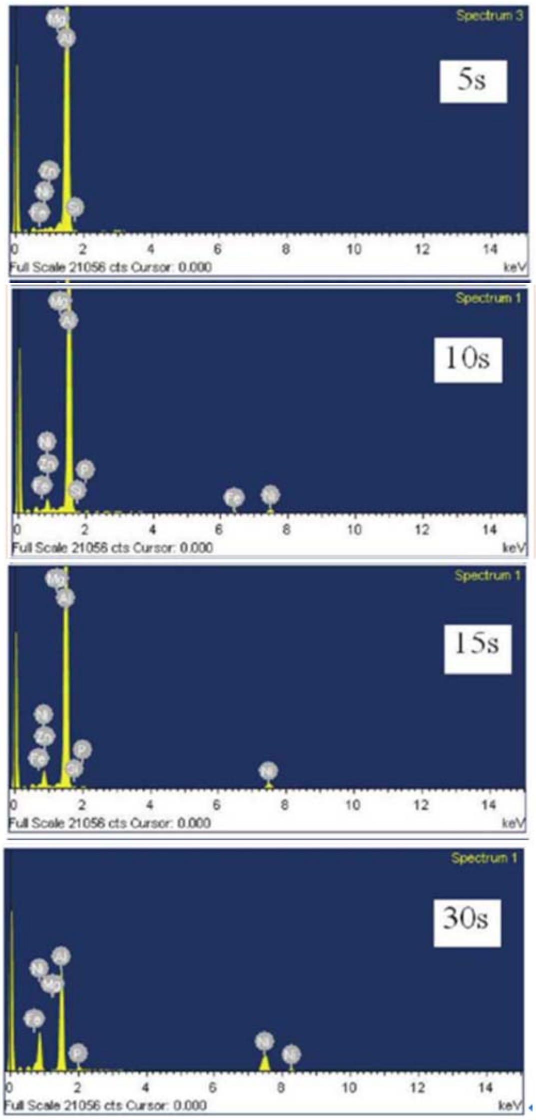


Figure 3: EDS spectra on electroless Ni-P alloy plating in different time, (1) 5 s; (2) 10 s; (3) 15s; (4) 30 s

Hardness is the resistance of a material to a fixed deformation caused by indentation, here the hardness refers to the Vickers hardness (HV), as can be observed from Table 3, the hardness of the Ni-P coating increases with the plating time, and when plating 90min, the hardness of the coating reaches 624.2HV0.2, which is 6 times of the Al6061 matrix material. It can be used to replace some precious metals, such as stainless steel.

3) Bond strength between acid plating Ni-P coating and substrate

Application of Ni-P coating is very extensive, but no matter what field, it must be a good combination between coating and substratein order to play the role of coating, if the binding force between the coating and the substrate is not good, its properties are almost all bad, such as coating easy to wrinkle, fall off and other phenomena, resulting in the product cannot be used normally.Therefore, the bonding strength between the coating and the substrate is an important part of the study of the coating properties.In this experiment, according to GB / T13913-92, using thermal shock test and file evaluation of the coating adhesion.When the samples were incubated in an electric furnace at 250℃±10℃for an hour, After being taken out, it was put into cold water immediately, repeated 20 times, and Ni-P in the coating did not separate from the aluminum alloy substrate, such as foaming and flaking.The specimen is secured to the vise and the end face is flattened with a flattened rasp, which is approximately 45°from the coating. The results show that there is no separation between the coating and the substrate and between the coating, indicating that the bond between the coating and the substrate is good.

4. Conclusion

1) After the alkali plating for different time, the Ni-P particles deposited on the surface of the sample were found to increase with the plating time, when the surface of the substrate is completely covered, the particles begin to aggregate, grow, fuse, and have a cellular structure on the surface.It is inferred that during the initial stage of electroless nickel plating, nickel-phosphorus particles were deposited near the Zn particles and deposited between the Zn particles and the first deposited Ni-P particles.
2) With the increase of electroless plating time, the thickness of the coating increases and the porosity decreases, when the coating thickness is 25μm, and the porosity is 0, the corrosion resistance of the sample is better, the roughness of the coating decreases as time becomes smaller and larger, which is due to the instability of the bath.The microhardness of the coatings increases with the time of electroless plating. The highest hardness of the coating is $624.2HV_{0.2}$, which can be used to replace some valuable metals and save resources.In performance test, this paper select the thermal shock experiments and file experiments to study the bonding strength of the coating and the substrate, there is no separation between the coating and the substrate in the experiment, so it can be concluded that there is a good adhesion between the coating and the substrate.

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